# Tropospheric methane retrieved from ground-based near-IR solar absorption spectra

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[1] High-resolution near-infrared solar absorption spectra recorded between 1977 and 1995 at the Kitt Peak National Solar Observatory are analyzed to retrieve column abundances of methane ($CH_4$), hydrogen fluoride (HF), and oxygen ($O_2$). Employing a stratospheric ''slope equilibrium'' relationship between $CH_4$ and HF, the varying contribution of stratospheric $CH_4$ to the total column is inferred. Variations in the $CH_4$ column due to changes in surface pressure are determined from the $O_2$ column abundances. By this technique, $CH_4$ tropospheric volume mixing ratios are determined with a precision of $\sim$0.5%. These display behavior similar to Mauna Loa in situ surface measurements, with a seasonal peak-to-peak amplitude of approximately 30 ppbv and a nearly linear increase between 1977 and 1983 of 18.0 ± 0.8 ppbv $yr^{-1}$, slowing significantly after 1990. *INDEX TERMS:* 0330 Atmospheric Composition and Structure: Geochemical cycles; 0394 Atmospheric Composition and Structure: Instruments and techniques; 1610 Global Change: Atmosphere (0315, 0325); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0325 Atmospheric Composition and Structure: Evolution of the atmosphere. **Citation:** Washenfelder, R. A., P. O. Wennberg, and G. C. Toon, Tropospheric methane retrieved from ground-based near-IR solar absorption spectra, *Geophys. Res. Lett.*, *30*(23), 2226, doi:10.1029/2003GL017969, 2003.

## 1. Introduction

[2] Methane ($CH_4$) is the most abundant hydrocarbon in the atmosphere and plays an important role in both radiative and chemical processes. Between 1984 and 1996, the globally averaged $CH_4$ mole fraction increased from $\sim$1625 to 1730 parts per billion by volume (ppbv) [*Dlugokencky et al.*, 1998]. Although the rate of increase is slowing, the cause of the variability has not been fully explained. Additional constraints on $CH_4$ sources and sinks are necessary to understand current behavior and to predict future trends.

[3] Active in situ monitoring programs are in place, including those undertaken by the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (NOAA CMDL) [*Dlugokencky et al.*, 1998] and the Global Atmospheric Gases Experiment/Advanced Global Atmospheric Gases Experiment (GAGE/AGAGE) [*Cunnold et al.*, 2002]. Although these measurements are highly accurate, they have limited spatial coverage.

[4] Space-based column measurements of $CH_4$ using scattered sunlight in the near-infrared (near-IR) have been proposed (e.g., SCIAMACHY and MOPITT) as a means of providing better spatial coverage. The near-IR region is a good candidate for space-based remote sensing because (i) it is near the peak of the solar Planck function; (ii) the column averaging kernels peak at the surface, facilitating identification of $CH_4$ sources and sinks; (iii) thermal emission from the atmosphere and instrument are negligible compared with reflected sunlight, simplifying calibration and radiative transfer calculations. Unfortunately, $CH_4$ spectroscopy is poorly characterized in this region and suffers from both missing weak lines and incomplete quantum assignments [*Brown*, 1992]. In this letter, we examine solar absorption spectra from the Kitt Peak National Solar Observatory to determine the suitability of the $2\nu_3$ band centered at 6001 $cm^{-1}$ for remote sensing of tropospheric $CH_4$.

[5] This analysis provides a long-term $CH_4$ column time series beginning in 1977. Sampling of $CH_4$ by the NOAA CMDL network did not begin until 1983 and GAGE/AGAGE network measurements were not initiated until 1985. Flask samples [e.g., *Blake and Rowland*, 1986; *Khalil and Rasmussen*, 1983] extend the record back to the mid-1970s. The scarcity of frequent, high precision measurements between 1977 and 1983 makes the Kitt Peak dataset especially valuable.

## 2. Determination of Tropospheric $CH_4$

[6] Column $CH_4$ exhibits variability driven by (i) changes in surface pressure, (ii) changes in the tropospheric $CH_4$ volume mixing ratio (VMR), and (iii) changes in the amount of stratospheric $CH_4$ due to changes in tropopause altitude. The $CH_4$ mole fraction decreases significantly in the stratosphere due to oxidation by $O(^1D)$, OH, and Cl. A 30 ppbv change in tropospheric $CH_4$ or a 30 hPa change in tropopause altitude will each produce $\sim$1.5% variation in the sea level $CH_4$ column. Thus, to accurately determine the tropospheric $CH_4$ VMR, it is necessary to correct for variations in both surface pressure and stratospheric contribution.

[7] Analysis of the pressure-broadened lineshape is commonly used to gain altitude information for gases retrieved in the mid-IR. However, this method is not optimal for the near-IR Kitt Peak spectra. For a typical $CH_4$ line at


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6000 $cm^{-1}$, the Doppler width exceeds the air-broadened width at ~14 km, preventing retrieval of stratospheric profile information. In addition, profile retrievals are limited by the spectral resolution of the available Kitt Peak measurements (typically $\delta\nu$ = 0.02 $cm^{-1}$), knowledge of the instrument lineshape, and lack of accurate air-broadening parameters for the $CH_4$ $2\nu_3$ band.

[8] In this analysis, we instead use simultaneous column measurements of HF to more accurately quantify stratospheric $CH_4$ variations. Previous studies have demonstrated that HF and $CH_4$ are inversely correlated in the stratosphere [*Luo et al.*, 1995]. As stratospheric air ages and $CH_4$ is oxidized, the photolysis of chlorofluorocarbons (CFC) initiates a chain of reactions, eventually yielding F atoms which react with $H_2O$ and $CH_4$ to form HF in the stratosphere.

[9] Provided the relationship between the $CH_4$ and HF VMRs is sufficiently linear, the $CH_4$-HF slope in the stratosphere can be applied directly to correct the $CH_4$ total column for stratospheric variations. Mathematically, this argument is shown by:

$$CH_{4\,VMR} = a + b \times HF_{VMR},\ b = \frac{\partial(CH_{4\,VMR})}{\partial(HF_{VMR})}. \quad (1)$$

The integrated column is:

$$X_{column} = \int_0^{Ps} X_{VMR} dp \quad (2)$$

with pressure (p) in units of molecules $cm^{-2}$ and $P_s$ equal to surface pressure. Therefore, by substitution:

$$CH_{4\,column} = \int_0^{Ps} (a + b \times HF_{VMR}) dp = a \times P_s + b \times HF_{column}. \quad (3)$$

Since $HF_{VMR}$ = 0 in the troposphere, parameter $a$ in (1) is equal to the tropospheric $CH_4$ VMR, assuming that $CH_4$ is well-mixed in the troposphere. Because the atmospheric $O_2$ VMR (0.2095) is highly constant, the relationship $O_{2\,column} = 0.2095 \times P_s$ can be used to eliminate $P_s$ from (3) yielding:

$$CH_{4\,trop\,VMR} = a = \frac{0.2095 \times (CH_{4\,column} - b \times HF_{column})}{O_{2\,column}}. \quad (4)$$

Equation (4) includes both the surface pressure correction using $O_{2column}$ and the stratospheric correction using $HF_{column}$. Dividing by $O_{2column}$ also removes possible systematic errors in the spectra, temperature profile, or calculated airmass that are common to $CH_4$, HF, and $O_2$. This equation implicitly assumes that $CH_4$ and HF have similar averaging kernels in the stratosphere (see S3)[1]. In this letter, we determine tropospheric $CH_4$ VMRs by simultaneously retrieving $CH_4$, HF, and $O_2$ columns from the Kitt Peak solar spectra and by employing two additional datasets to determine the stratospheric $CH_4$-HF relationship, b, and its time dependence.

## 3. The Kitt Peak Spectra

[10] The spectra analyzed in this work have been described previously [*Yang et al.*, 2002]. The dataset includes more than 400 high-resolution near-IR solar absorption spectra ($\delta\nu$ = ~0.02 $cm^{-1}$) obtained with the 1-m Fourier transform spectrometer (FTS) at the McMath telescope complex of the Kitt Peak National Solar Observatory (31.9 N, 111.6 W, 2.09 km above sea level) between 1977 and 1995. Each of these spectra include the 4000–8000 $cm^{-1}$ region necessary for the simultaneous retrieval of $CH_4$, $O_2$, and HF. Many of these observations were used by *Wallace and Livingston* [1990] to determine the column-averaged dry air VMR of $CH_4$ and $CO_2$. Their work used equivalent widths to analyze 12 manifolds of the $2\nu_3$ $CH_4$ ($\nu_0$ = 6001 $cm^{-1}$) band and 14 lines of the $O_2$ 0-0 $^1\Delta_g - {}^3\Sigma_g^-$ ($\nu_0$ = 7882 $cm^{-1}$) band.

[11] Here, we reanalyze the Kitt Peak solar spectra using an improved spectral retrieval algorithm with updated spectroscopic linelists for $CH_4$, $O_2$, $H_2O$, and solar absorption lines. We simultaneously fit the entire $O_2$ band (containing more than 200 significant lines), the $CH_4$ $2\nu_3$ P-branch (containing ten significant manifolds), and the strong HF R(1) (1-0) line at 4038.96 $cm^{-1}$.

## 4. Spectral Analysis and Retrievals

[12] The line-by-line fitting algorithm used in this work (GFIT) was developed at the Jet Propulsion Laboratory (JPL) for the analysis of solar absorption spectra. The use of the GFIT algorithm, temperature profiles for Kitt Peak, $O_2$ spectral parameters, and solar linelist have been described previously [*Yang et al.*, 2002]. The atmospheric $CH_4$ and HF a priori VMR profiles are based on JPL MkIV measurements recorded during balloon flights from Ft. Sumner, New Mexico, and Daggett, California (both at ~34°N).

[13] Spectral parameters for the HF R(1) (1-0) line are taken from the HITRAN database [*Rothman et al.*, 1998]. Line position, intensity, and ground-state energy parameters for the $CH_4$ $2\nu_3$ manifolds [*Margolis*, 1988; *Margolis*, 1990] are taken from HITRAN, but different air-broadened widths are employed. Since measurements of $2\nu_3$ linewidths have never been reported, in HITRAN these lines are assigned air-broadened widths based on measurements of the $\nu_2$ and $\nu_4$ $CH_4$ bands [*Brown*, 1992]. When these parameters were used to fit laboratory and atmospheric spectra, however, the residuals showed that the assigned widths are systematically large. Additionally, $CH_4$ columns initially retrieved from the Kitt Peak spectra had unreasonably large, symmetric daily variations of about 6% that peaked at noon. In our retrieval of $CH_4$, we have substituted broadening parameters from the $\nu_3$ band as these are expected to be more closely related to the $2\nu_3$ band than the values assigned in HITRAN. (See S1 for a detailed discussion and linelist[1].) To further minimize the airmass dependence of the analysis, we fit only the P-branch (5880–5996 $cm^{-1}$). These manifolds are weaker than the R- and Q-branch manifolds, making this region less susceptible to errors in linewidth. The retrieved tropospheric $CH_4$ VMR is observed to vary by about 1% between 1 and 10 airmasses.

[1] Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2003GL017969.

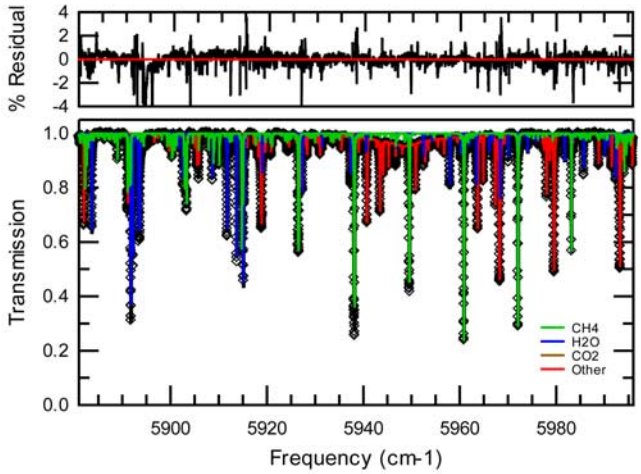


**Figure 1.** Example of a spectral fit to the 5880–5996 $cm^{-1}$ region, containing the $CH_4$ $2\nu_3$ P-branch, of a Kitt Peak spectrum measured at 70.94° SZA on 9 May 1981. Diamonds are the measurements and black lines are the fitted transmittance. Contributions from individual gases are shown in color.

[14] Fits to the $2\nu_3$ P-branch include a full range of ground-state energies, so retrieved column $CH_4$ is only weakly dependent on the assumed temperature profile (0.01% $K^{-1}$). Considering $O_2$ and HF temperature sensitivities as well (0.02% $K^{-1}$ and 0.26% $K^{-1}$ respectively), a systematic error of 5 K at all levels within a temperature profile would change the retrieved tropospheric $CH_4$ VMR in (4) by ~2 ppbv (~0.1%).

[15] A spectral fitting example for the $CH_4$ $2\nu_3$ P-branch is shown in Figure 1. A fit to the $O_2$ 0–0 $^1\Delta_g - {}^3\Sigma_g^-$ band ($\nu_0$ = 7882 $cm^{-1}$) has been shown previously in *Yang et al.* [2002] and a fit to the HF R(1) (1-0) line is included in S2[1]. The residuals (model-observed) are also illustrated in Figure 1. We have excluded from further analysis 32 observations (7.7%) that produce column errors greater than 3.0% for $O_2$ or $CH_4$, as estimated from the spectral residuals. An additional 94 observations (22.7%) that produce column errors greater than 9.0% for HF have also been eliminated. The remaining 288 spectra typically have column errors of 1.4–2.8% for $O_2$, 1.7–2.7% for $CH_4$, and 3.5–6.7% for HF. The required HF precision is modest, as it is used as a linear correction with relatively small sensitivity. A 30 hPa change in tropopause pressure results in a ~1.5% change in the $CH_4$ column, while the HF column changes by ~15%.

[16] The retrieved slant column amounts were divided by the calculated airmasses to determine vertical column amounts. The airmass calculation includes the 226 m optical path inside the telescope [*L. R. Brown*, private communication, 2002] and the effects of refraction. The column-averaged $CH_4$ VMRs (0.2095 × $CH_{4column}/O_{2column}$) without the HF correction described in (4) are shown in Figure 2a.

[17] Monthly average $CH_4$ flask data from NOAA CMDL's Mauna Loa site are also shown in Figure 2a. The dotted trend line through the May 1983 to 1995 data is the twelve-month running average. The average seasonal cycle is determined by subtracting the running average from the data and binning the results by month. No evidence has been found for changes in the amplitude of the $CH_4$ seasonal cycle [*Dlugokencky et al.*, 1997], so this approximation is reasonable. The trend prior to May 1983, for which no Mauna Loa flask data are available, is a linear extrapolation with a slope that is consistent with the reported global tropospheric $CH_4$ increase of 18 ± 2 ppbv $yr^{-1}$ during 1978 to 1983 [*Blake and Rowland*, 1986]. The average Mauna Loa seasonal cycle was then applied to the linear growth rate for 1977 to May 1983. The extrapolation of the seasonal cycle is used here only as a visual guide.

[18] The retrieved Kitt Peak column-average $CH_4$ VMRs are systematically lower (4%) than the Mauna Loa flask samples. Some of this difference is expected as the $CH_4$ VMR is lower in the stratosphere, but geographical differences and uncertainty in the absolute $CH_4$ line strengths and widths preclude meaningful comparison of the column-average $CH_4$ VMRs.

## 5. Tropospheric $CH_4$ Volume Mixing Ratios

[19] The column-average $CH_4$ VMRs in Figure 2a include significant variability driven by changes in tropopause altitude. This is illustrated by the anti-correlation of $CH_4$ in Figure 2a with retrieved HF columns in Figure 2b (see S3). In many years the HF column varies by as much as a factor of two between summer and winter. The seasonal variation in HF is superimposed on its increasing burden due to increasing CFC VMRs. Figure 2b shows the fluorine-

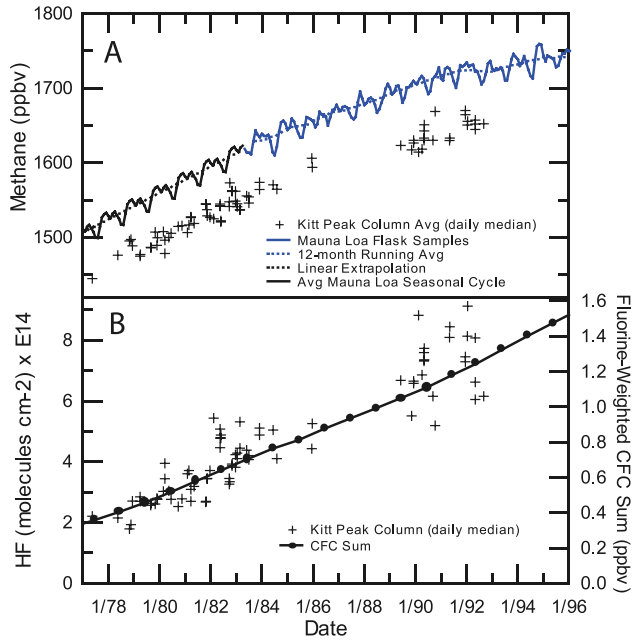


**Figure 2.** (a) Time series of Kitt Peak column-averaged $CH_4$, determined from 0.2095 × $CH_{4column}/O_{2column}$. Mauna Loa flask samples (monthly average) are shown with their twelve-month running average. No Mauna Loa flask data exists prior to May 1983. A linear extrapolation with slope 18.0 ppbv $yr^{-1}$ is shown for this period, with the average Mauna Loa seasonal cycle applied. (b) Time series of Kitt Peak column HF. The fluorine-weighted CFC sum (CFC-11 + 2 × CFC-12 + 3 × CFC-113 + 2 × HCFC-22) has been lagged by six years to account for atmospheric transport into the stratosphere.

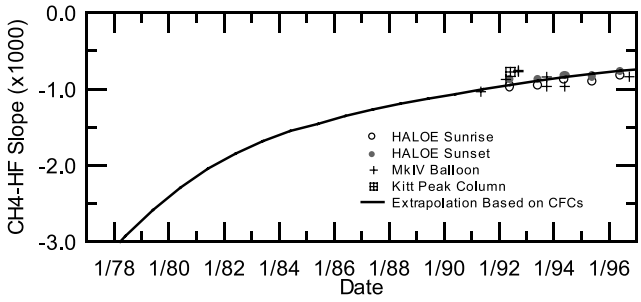


**Figure 3.** $CH_4$-HF slope values, b, obtained from the HALOE, MkIV, and Kitt Peak data. Slope values have been extrapolated back to 1977 using the CFC sum shown in Figure 2b.

weighted CFC trend (CFC-11 + 2 × CFC-12 + 3 × CFC-113 + 2 × HCFC-22) reconstructed from measurements by the ALE/GAGE/AGAGE network at Cape Grim, Tasmania. The fluorine-weighted CFC sum is lagged by six years to account for atmospheric transport within the stratosphere. Further details are given in S3[1].

[20] To retrieve the tropospheric $CH_4$ VMR using (4), the correlation of $CH_4$ with HF, b, is needed. This slope is determined here from two datasets. The Halogen Occultation Experiment (HALOE) instrument on the Upper Atmosphere Research Satellite (UARS) has been measuring $CH_4$ and HF simultaneously in solar occultations since 1991 using the gas filter correlation technique [*Russell et al.*, 1993]. The $CH_4$-HF plots for that data are characterized by tightly fitted curves for different latitude bands [*Luo et al.*, 1995]. Using sunrise and sunset data measured at tangent latitudes of 20–40°N, we have fitted a linear $CH_4$-HF relationship. The second $CH_4$-HF dataset was recorded by the JPL MkIV Interferometer during 8 balloon flights at tangent latitudes between 32–38°N during 1990 to 1996. The MkIV is an FTS that uses the solar occultation technique to record mid-IR spectra [*Toon*, 1991].

[21] Figure 3 shows the slope of the $CH_4$-HF correlation, b, obtained from the HALOE and MkIV data for pressure levels between 10 and 100 hPa. The value calculated from the retrieved Kitt Peak $CH_4$ and HF columns is also shown. The $CH_4$-HF slope has increased significantly between 1977 and 1995, due to increasing HF VMRs. The slope has been extrapolated back to 1977 using the time-lagged VMR of fluorine-weighted CFCs, shown in Figure 2b. Although this extrapolation is not ideal, it is necessary due to the lack of simultaneous $CH_4$ and HF profile measurements available from the 1970s and 1980s. Further explanation of the HALOE, MkIV, and Kitt Peak b values, as well as extrapolation of b using CFC data is given in S3[1].

[22] Tropospheric $CH_4$ VMRs calculated from (4) are shown in Figure 4a and provided in tabular form in S3. The Mauna Loa data in Figure 4a are identical to those in Figure 2a. The Kitt Peak tropospheric $CH_4$ VMRs are scaled by 1.015 to bring their values into agreement with the Mauna Loa data. This scaling was empirically determined to minimize bias between the Kitt Peak and Mauna Loa data. The linear slope of the 1977 to 1983 Kitt Peak tropospheric VMRs is 18.0 ± 0.8 ppbv $yr^{-1}$, consistent with the value of 18 ± 2 reported by *Blake and Rowland* [1986] for this period.

[23] The average seasonal cycle (and 2σ variability) for the 1983 to 1995 Mauna Loa data is shown in Figure 4b. The Kitt Peak data were detrended by subtracting the linear trend and twelve-month running average shown in Figure 4a. Figure 4b shows that approximately ±2% seasonal variation is evident in the Kitt Peak data, consistent with the Mauna Loa data.

## 6. Conclusions

[24] Reanalysis of the high-resolution near-IR spectra obtained at the Kitt Peak National Solar Observatory demonstrates that tropospheric $CH_4$ VMRs can be retrieved with 0.5% precision. However, our results are limited by current $CH_4$ spectroscopy (linewidths, intensities, and missing weak lines) and by our ability to accurately separate tropospheric and stratospheric variability using (4). The largest errors in this analysis include noise in our HF retrievals, the assumption of a linear $CH_4$-HF relationship in the stratosphere, and the difficulty of extrapolating this relationship into the past. Despite these challenges, reanalysis of the Kitt Peak spectra allows the tropospheric $CH_4$ record to be extended back to 1977. These results show that high precision measurements of column $CH_4$ are possible using ground-based FTS, and that this technique can be used to validate future space-based observations. However, to determine $CH_4$ sources and sinks from column measure-

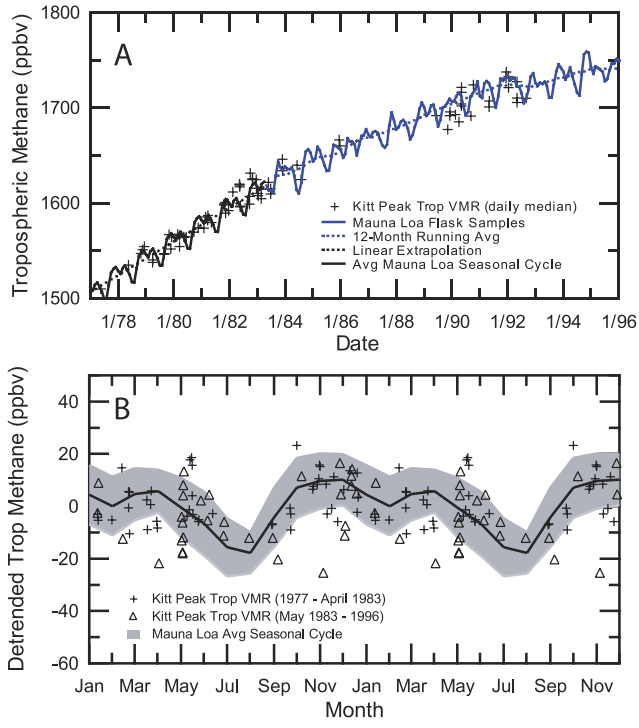


**Figure 4.** (a) Time series of Kitt Peak tropospheric $CH_4$ VMR, determined from (4). The data have been multiplied by 1.015 (see text) to bring them into agreement with the Mauna Loa data. (b) Detrended Kitt Peak tropospheric $CH_4$ VMR shown together with the average Mauna Loa seasonal cycle (2σ variability). Kitt Peak data prior to May 1983 are represented by crosses and later data are represented by triangles.

ments, it will be necessary to separate the tropospheric and stratospheric column contributions. This letter uses HF as a stratospheric tracer to achieve this separation. In the future, higher resolution spectra and precise laboratory measurements of air-broadened widths may allow direct retrieval of tropospheric $CH_4$ VMRs.

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## References

Blake, D. R., and F. S. Rowland, World-wide increase in tropospheric methane, 1978–1983, *J. Atmos. Chem.*, *4*, 43–62, 1986.

Brown, L. R., Methane and its isotopes: Current status and prospects for improvement, *J. Quant. Spectrosc. Ra.*, *48*, 617–628, 1992.

Cunnold, D. M., L. P. Steele, and P. J. Fraser, et al., In situ measurements of atmospheric methane at GAGE/AGAGE sites during 1985–2000 and resulting source inferences, *J. Geophys. Res.*, *107*(D14), doi:10.1029/2001JD001226, 2002.

Dlugokencky, E. J., K. A. Masarie, P. M. Lang, and P. P. Tans, Continuing decline in the growth rate of the atmospheric methane burden, *Nature*, *393*, 447–450, 1998.

Dlugokencky, E. J., K. A. Masarie, and P. P. Tans, et al., Is the amplitude of the methane seasonal cycle changing?, *Atmos. Environ.*, *31*, 21–26, 1997.

Khalil, M. A. K., and R. A. Rasmussen, Sources, sinks, and seasonal cycles of atmospheric methane, *J. Geophys. Res.*, *88*, 5131–5144, 1983.

Luo, M., R. J. Cicerone, and J. M. Russell III, Analysis of Halogen Occultation Experiment HF versus $CH_4$ correlation plots: Chemistry and transport implications, *J. Geophys. Res.*, *100*(D7), 13,927–13,937, 1995.

Margolis, J. S., Measured line positions and strengths of methane between 5500 and 6180 cm-1, *Appl. Opt.*, *27*, 4038–4051, 1988.

Margolis, J. S., Empirical values of the ground state energies for methane transitions between 5500–6150 cm-1, *Appl. Opt.*, *29*, 2295–2302, 1990.

Rothman, L. S., et al., The HITRAN molecular spectroscopic database and HAWKS (HITRAN atmospheric workstation): 1996 edition, *J. Quant. Spectrosc. Ra.*, *60*, 665–710, 1998.

Russell, J. M., L. L. Gordley, and J. H. Park, et al., The Halogen Occultation Experiment, *J. Geophys. Res.*, *98*(D6), 10,777–10,797, 1993.

Toon, G. C., The Jet Propulsion Laboratory MkIV Interferometer, *Opt. Photonics News*, *2*, 19–21, 1991.

Wallace, L., and W. Livingston, Spectroscopic observations of atmospheric trace gases over Kitt Peak: 1. Carbon dioxide and methane from 1979 to 1985, *J. Geophys. Res.*, *95*(D7), 9823–9827, 1990.

Yang, Z., G. C. Toon, J. S. Margolis, and P. O. Wennberg, Atmospheric $CO_2$ retrieved from ground-based near IR solar spectra, *Geophys. Res. Lett.*, *29*(9), 1339, 10.1029/2001GL014537, 2002.

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